Direct resolution of unoccupied states in solids via two photon photoemission

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Abstract

Non-linear effects in photoemission are shown to open a new access to the band structure of unoccupied states in solids, totally different from hitherto used photoemission spectroscopy. Despite its second-order nature, strong resonant transitions occur, obeying exact selection rules of energy, crystal symmetry, and momentum. Ab-initio calculations are used to demonstrate that such structures are present in low-energy laser spectroscopy experimental measurements on Si previously published. Similar resonances are expected in ultraviolet angle-resolved photoemission spectra, as shown in a model calculation on Al.

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Our understanding of the electronic properties of materials has spectacularly progressed in the last decade. The spread of theoretical methods based on first principles, together with the development of novel and sophisticated experimental techniques, have led to accurate descriptions of the ground state in many condensed matter systems. In particular, experimental techniques based on the photoemission of electrons from the sample currently are the dominant tool to understand solids and lower dimensional systems in terms of their electronic structure.

In contrast, a major challenge remaining in condensed matter physics is the description of excited electronic states at the same level of accuracy reached in the description of the ground state. From the experimental point of view, information is limited: A momentum resolved direct band structure spectroscopy for unoccupied states is available only through inverse photoemission spectroscopy (IPS) [1, 2]. Despite a long history, IPS has never attained an accuracy comparable to that of angle-resolved photoemission (ARPES) [3, 4] for occupied states. Other methods, such as electron diffraction at very low energies [5], are rather indirect. Furthermore, these methods are affected by the break of three dimensional symmetry brought forth by the surface: A direct access to the band structure of the solid is thus prevented because of the cumbersome momentum non-conservation.

However, a new generation of broadly tunable light sources of high intensity has been developed and can dramatically alter such situation. Multiphoton processes can be the key to study electronic excited states. Investigation of localized states, as e.g. surface and image states, with two-photon excitation has already attracted much interest [6]. Pump-probe techniques have been extensively employed for the study of electron and adsorbate dynamics [7, 8]. The spectroscopy of bulk electronic structure of the continuum by two-photon processes has received comparatively little attention [9, 10, 11, 12, 13]. The role of intermediate unoccupied states in these transitions has not been fully understood yet. Theoretical models on this issue mainly rely on density matrix time evolution [14, 15] and non-linear response treatments [16]. In a full theory, the dynamical properties of the system should be described at the same level of accuracy provided by the one-step model of one-photon photoemission based on *ab-initio* calculations. The work that we present in this Letter is a necessary first step along this direction.

We here develop and justify a band-mapping procedure for unoccupied states in bulk, which surpasses the inaccuracies and drawbacks of the standard traditional mapping proce-

dures. It is based on non-linear effects appearing in the photoemission process and on the subsequent appearance of non-linear resonant peaks in the photoemission spectra. Because of their narrowness, these peaks should be easier to detect with tunable light sources of low bandwidth. Starting from the one-step model, we show that the monochromatic two-photon photoemission yields directly the energy difference between an occupied state and an unoccupied state, within the theoretical accuracy of the linewidths of the participating states. The momentum identification is unique in surface parallel as well as in perpendicular direction for the initial to intermediate transition. The bands involved in the transition are assigned through symmetry selection. The range of application of the scheme is far reaching, as it opens a new access to the band structure of unoccupied states in solids. To prove our point, we analyze here two different sets of experimental photoemission spectra in Si [9, 10], and bring them together under one common interpretation.

We theoretically investigate contributions to the photoemission spectra of orders higher than linear in the perturbation expansion with respect to the photon intensity. We restrict the considerations here to the lowest order correction and obtain the probability per unit of time of accepting an electron in the detector (i.e., the photocurrent $J = J_{1phot} + J_{2phot}$) for transitions from a definite initial state $|a\rangle$ to a final state $|f\rangle$. The latter is specified by energy E_k^f and momentum k. It has to be summed over occupied initial single particle states (momentum k_a and energy $E_{k_a}^a$) and unoccupied intermediate states (k_z and $E_{k_z}^z$).

$$
\begin{aligned}
J \; \propto \; & \sum_{k_a \leq k_F} |h_{fa}|^2 \, \delta(E_k^f - E_{k_a}^a - \hbar\omega) \\
& + \frac{1}{4} \sum_{k_a \leq k_F} \delta(E_k^f - E_{k_a}^a - 2\hbar\omega) \left| \sum_{k_z} \frac{h_{fz} h_{za}}{E_{k_z}^z - E_{k_a}^a - \hbar\omega - i\eta} \right|^2
\end{aligned}
\tag{1}
$$

To obtain the above formula, real one-photon second-order emission processes are disregarded. The transition matrix elements are represented by h_{ik}. The sum runs over intermediate states $|z\rangle$ reached by virtual one-photon transitions from the initial state observing Pauli exclusion principle. Compared with bulk band structure investigations by one-photon photoemission such transitions are very special because full three-dimensional momentum is conserved[17]. It is this property which promises a large step forward in photoemission spectroscopy. First, because it allows the access to unoccupied states. Second, because it reaches the maximum resolution provided by first principles theories.

The meaning of η in Eq. (1) is two-fold: First, it represents the decay width of the

intermediate state as a lifetime and the dephasing of the transition amplitude owing to intrinsic elastic and inelastic processes (η_0). Second, the strong external photon field may broaden the energies by its ponderomotive force in high-intensity light sources (η_1). Thus, $\eta = \eta_0 + \eta_1$ makes J finite for all η in Eq. (1). The ratio R between the two-photon and one-photon currents can be approximated by $R(E_0) = \left| \frac{eE_0 a}{\eta} \right|^2$, with a being the lattice constant, e the electron charge, and E_0 the external field.

From the expression above, we can get the order of magnitude of the two-photon vs. one-photon current R. The decay width η is below 1 eV for intermediate states near the vacuum level. Typical values of E_0 for Ti:sapphire laser systems range from $\approx 10^6$ V/m [13] to $\approx 10^{10}$ V/m [18, 19]. The corresponding ratio is $R = 0.2 \times 10^{-6}/\eta^2$ to $R = 0.2 \times 10^2/\eta^2$ respectively (with η in eV), and higher for a free electron laser. The latter is at the borderline of perturbation theory validity. Hence, even for the smaller laser intensity, the ratio of two-photon to one-photon intensity is still significant for small broadening widths of some meV. In the following, and for the sake of a working order of magnitude, we take $R = 0.2 \times 10^2/\eta^2$ and use η as input parameter.

As a first application of our formalism, we focus into photoemission processes triggered by strong optical laser fields in the femtosecond range. We address here two-photon photoemission processes from the technologically significant Si(001) semiconductor surface. Resonant photoexcitation in this surface has been already observed experimentally [9, 10]. In Ref. 9, a two-photon bulk transition was identified. The strong enhancement of the photocurrent, with a peak width of 0.3 eV [9], must be attributed entirely to an intermediate state. Furthermore, a strong peak from a two-photon process is observed in Ref. 10 as a transition from the $\Delta_{2'}$ valence band to the Δ_5 conduction band. This structure could be a candidate for the transitions discussed here as well. In any case, we remark that isolated single resonances are not required for our analysis. In dispersing bands, the required energy matching between the photon energy and each one of the electron transitions is not rare. This will increase the number of cases with matching conditions, as well as a a broadening of the peaks.

We first calculate the Si band structure, which is plotted in Fig. 1, using density functional theory (DFT) and the augmented plane wave (APW) formalism [20]. The two-photon photocurrent, also shown in Fig. 1 for two different values of photon energy, is obtained from this DFT calculation as well. Initial and intermediate states are scattering states,

which can be represented by Bloch waves (bulk wave functions) incident from the interior of the crystal and scattered by the surface. In addition, surface states, which are not related to any bulk solutions may appear among initial and intermediate states. Because we are interested only in the asymptotics of the final state at the detector, the summation over the final states reduces to the calculation of the time-reversed LEED function, similar to the first order one-step theory. The LEED state is calculated ab-initio assuming a step-like surface barrier and an optical potential V_i. In calculating the squared modulus of the matrix element h_{za}, we sum up incoherently over all Bloch constituents, thus assuming an absolutely rough surface. The matrix elements h_{zf} are assumed to depend only on the momentum difference $k_f - k_z$, through a Lorentzian function.

Figure 1 shows that distinct peaks in the two-photon photocurrent are associated with initial to intermediate state resonances, corresponding to momentum conserving transitions. In addition, the spectra show larger enhancements when the final state is a strong current carrying wave. This is further illustrated by the ab-initio calculations of the two-photon photocurrent for the Si(001) surface, shown in Fig. 2. The theoretical photocurrent of Fig. 2 very much resembles that measured in Ref. 9, assuming an overall shift of the theoretical unoccupied states by 0.3 eV to higher energy, within the picture of a scissor operator. Applying the scissor operator, one can see that the maximum of the photocurrent peaks shifts by approximately 0.15 eV, to photon energy of 3.95 eV, as in experiment. The binding energies given by the peaks themselves then align, too. This proves the possibility to precisely adjust the energies to experiment.

The calculated peak magnitude and dispersion are shown in Fig. 3 and compared to the corresponding measured magnitudes [9, 10], finding good agreement as well. The energy analysis shows an almost linear final state energy vs. photon energy behavior. A kink is predicted at the photon energy for which the maximum peak intensity is found. This is precisely the energy at which the LEED state starts to play a role in the two-photon photocurrent.

In addition to laser-based techniques, other standard photoemission techniques, such as ARPES, can benefit from the analysis proposed in this Letter. For illustration purposes, we show in the following a model calculation on Al(111), in which photoemission spectra are obtained from a similar one-step calculation. We represent the Al(111) surface by a one-dimensional model in which the initial and intermediate states are tight binding orbitals

and the final states are nearly free electron waves. Only one branch of the final state bands, which correspond to the LEED complex band structure that allows electron escape, is considered. We also use this system to discuss the expected magnitude of the non-linear peaks, as compared to the one-photon peaks.

Figure 4 shows both the two-photon photocurrent (with $\eta = 0.1$) and the one-photon current of doubled frequency. The final state is the same for both types of photoemission. In each two-photon spectrum, a very narrow peak appears and dominates the spectrum by orders of magnitude. It comes from rather sharp transitions from the initial to the intermediate state (denoted by rectangles), given by the Lorentzian function in Eq. (1), which has the same shape as an exactly direct transition at a definite momentum. The intermediate to final state transition is often obscured by the non-conservation of perpendicular momentum. If, by chance, it is conserved too, a resonant magnification of the peak occurs. In Fig. 4, this happens for $2\hbar\omega = 25.5$ eV and $2\hbar\omega = 40$ eV.

Furthermore, in the example of the $2\hbar\omega = 35.2$ eV curve in Fig. 4, the rectangle shows the main peak resonance occurring at a momentum different from the usual one-photon direct transition into the final state parabola. As a consequence, the current is significantly reduced as compared to the transitions that fully conserve energy and momentum. A side peak arises at conserved momentum between the initial and final states (denoted by circles), as in one-photon spectra. The intermediate energy is not at its resonance, however. Without exceptions, the initial and final energies are sharp because of the δ-function in Eq. (1).

Summarizing, we propose a new methodology to extract momentum-resolved band-structure information for unoccupied electron states in bulk. The non-linear contributions of the two-photon photoemission experimental spectra are used for this purpose. We show that the composition of a bulk two-photon spectrum displays the clear fingerprint of a Lorentzian line at exact momentum conservation for the transition between initial and intermediate state. It allows a direct association of both contributing bands and the determination of their energy difference at that specific momentum if the bands are unique. A standard Lorentzian deconvolution is necessary in the case of multiple bands. Experimental results for low photon energies on Si(001) support the theoretical findings. With respect to explore and utilize these effects in ARPES, the counter-play between higher light intensity (higher photocurrent) and the concomitant broadening of the initial to intermediate state transition by ballistic acceleration has to be considered. Furthermore, a dispersion of the initial band

sufficient to fix the momentum of that transition is needed.

Within this methodology, the values of fundamental band gaps in semiconductors appear as direct results of the two-photon spectra. These results represent the optical direct band gaps at any momentum where the transition via an intermediate state is observed. They are in contrast with band gaps of direct and inverse photoemission where the particle number is not conserved. Within the same reasoning, the scissors operator, which rather artificially separates energetically excited bands from the ground state, can be quantified. In Si(001), for instance, the shift of excited bands to higher energies by the real part of the self-energy could be adjusted to experiment as 0.3 eV. This shift seems to account for both a quasiparticle shift upwards and an excitonic shift downwards.

Let us finally remark that non-linear optical processes in atoms and molecules have been crucial in the discovery and understanding of new physical phenomena in recent years. A similar burst for condensed matter systems can be envisaged in the years to come. We hope that the novel resonant processes proposed in this Letter can serve as an additional motivation to theorists and experimentalists alike to further explore the exciting capabilities of non-linear spectroscopies in solids.

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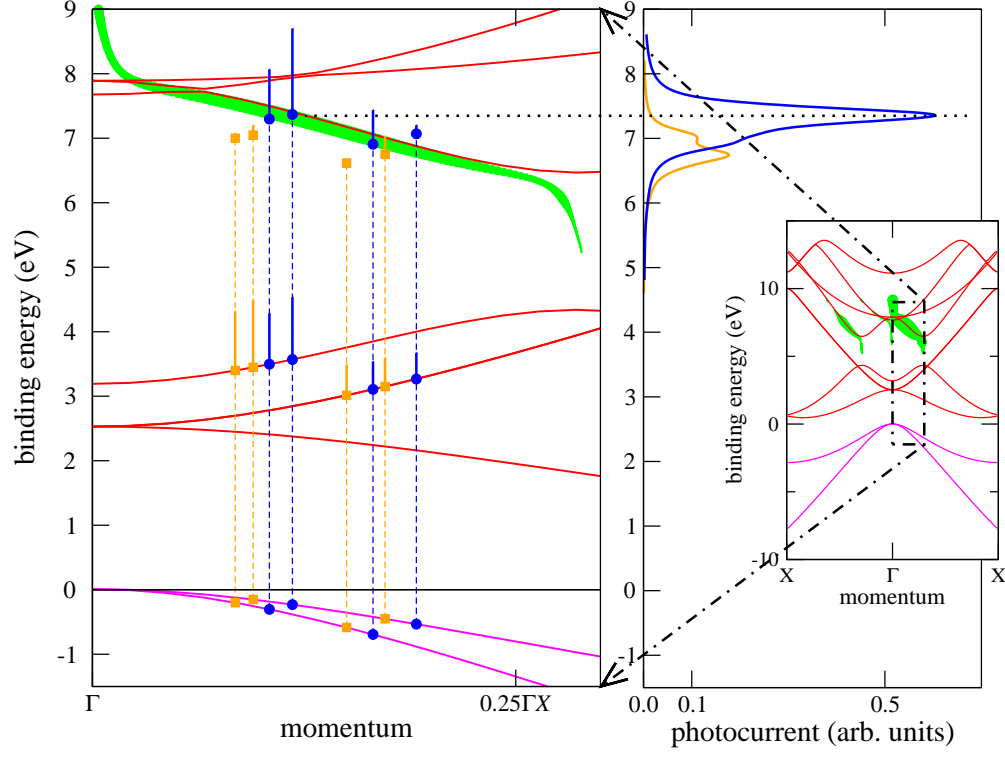
FIG. 1: (Color online) Two-photon photocurrent and some relevant two-photon transitions in Si(001). Right panel: Photocurrent vs. binding energy. Yellow (blue) spectrum corresponds to 3.6 (3.8) eV photon energy. The full band structure is shown in the inset as well. Thickened green lines denote LEED states in the complex band structure and the thickness gives the coupling strength to the vacuum of that band. Left panel: Magnified view of a reduced portion of the band structure that contributes to the photocurrent. The transitions are indicated by squares and circles for 3.6, 3.8 eV photon energy, respectively. LEED states denoted as in right panel. Vertical solid lines rising from the squares and circles show the magnitude of the coupling matrix element for this transition.
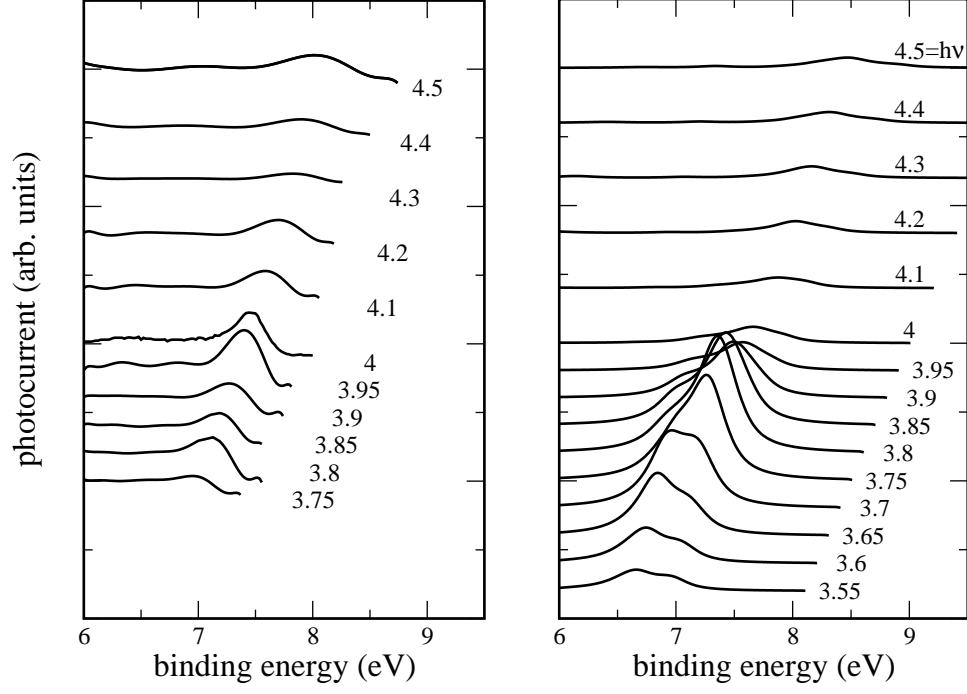
FIG. 2: Two-photon spectra from Si(001). Left panel: Experimental values [9] for $\hbar\omega = 3.75$ to 4.5 eV. Right panel: one-step calculation for $\hbar\omega = 3.55$ to 4.5 eV, with broadening $\eta = 0.15$ eV for initial and intermediate states, and optical potential $V_i = 0.125$ eV.
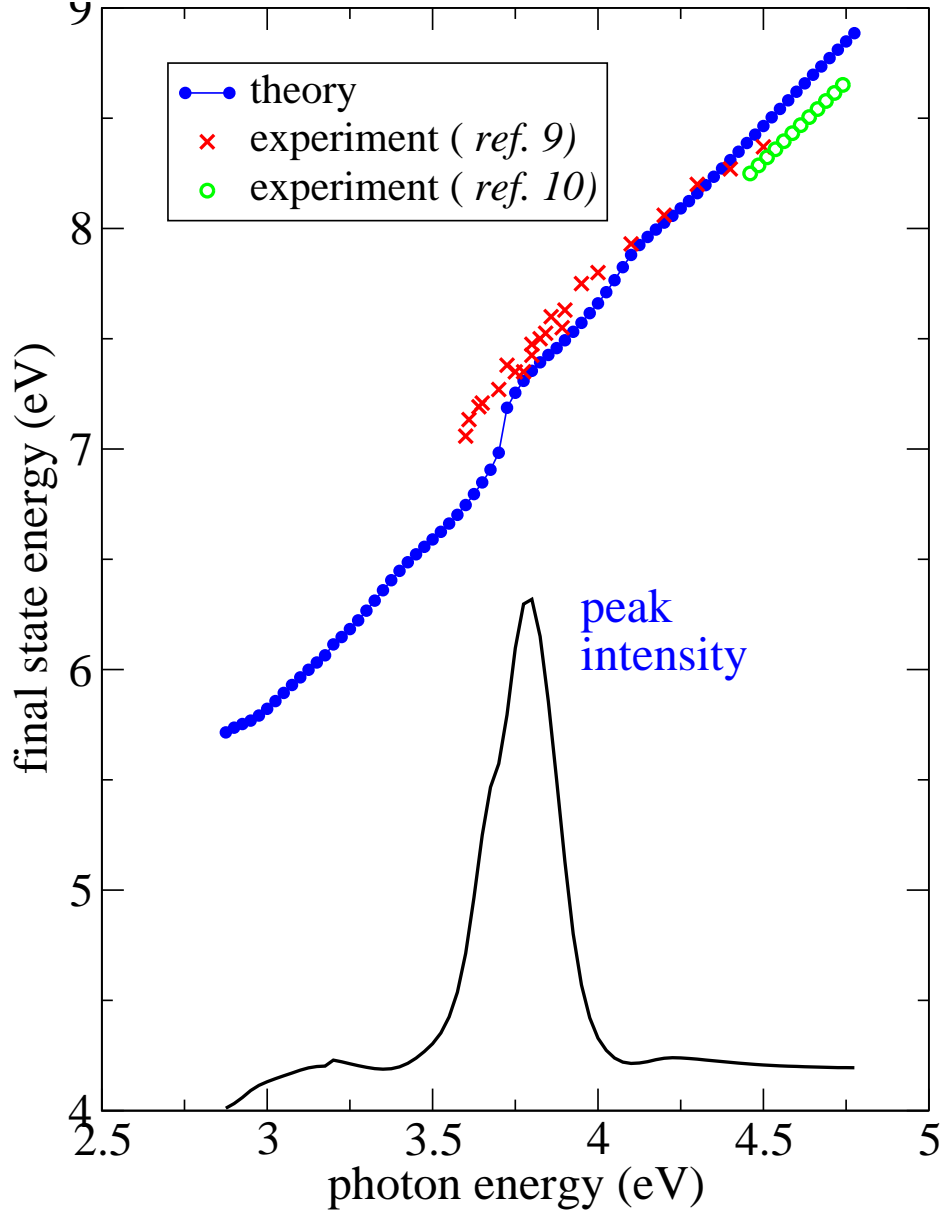
FIG. 3: (Color online) Peak magnitude and dispersion in the two-photon spectra of Si(001). Calculated (full blue circles) peak positions are shown as a function of photon energy. Experimental values of Ref. [9] (red crosses) and Ref. [10] (open green circles) are shown as well. Solid black curve shows the theoretical peak height in arbitrary units.
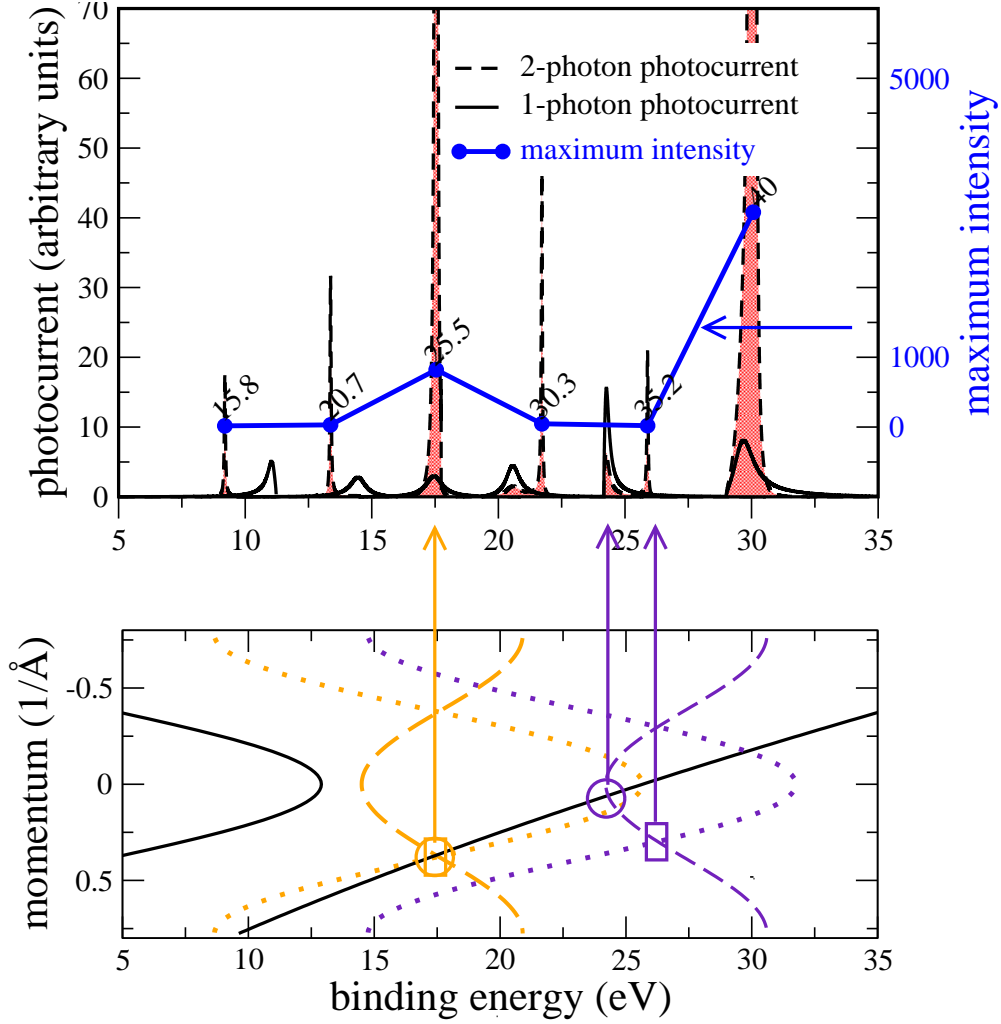
FIG. 4: (Color online) Upper panel: Two-photon (broken lines) and one-photon (solid lines) photocurrents for Al(111) (left ordinate), vs. binding energy. The maximum intensity values for the two-photon current are also plotted as blue circles (right ordinate), linked with a line to guide the eye. Numbers over these circles denote twice the photon energy, in units of eV. One-photon transitions are associated with doubled photon frequency. Lower panel: Momentum vs. binding energy of model band structure (solid lines). Two particular cases [$2\hbar\omega = 25.5$ (orange) and 35.2 eV (purple)] are associated by arrows with the corresponding peaks in the spectra above. The initial band has been shifted by $2\hbar\omega$ (broken lines) and the intermediate state band has been shifted by $1\hbar\omega$ (dotted lines). Rectangles (circles) denote conservation of momentum between initial and intermediate (initial and final) states.